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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

APR - 4 1991

OFFICE OF  
PESTICIDES AND TOXIC  
SUBSTANCES

**MEMORANDUM**

SUBJECT: Chlorpyrifos. Amended label for Lock-On\* to include alfalfa in Arizona and California. EPA Reg. No. 62719-79. DEB #7627. MRID No. 417390-01.

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TO: Dennis Edwards (PM-12)  
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DowElanco requests a label amendment for Lock-On\* insecticide to include alfalfa, with a PHI of 4 days, for Arizona and California. The active ingredient is chlorpyrifos, O,O-Diethyl O-(3,5,6-trichloro-2-pyridyl)-phosphorothioate. Tolerances for combined residues of chlorpyrifos and its 3,5,6-Trichloro-2-pyridinol (TCP) metabolite have been established for alfalfa, green forage, 4 ppm, and alfalfa, hay, 15 ppm (40 CFR §180.342). A tolerance is pending for alfalfa (PP#3F2884) in which the levels of chlorpyrifos and TCP are expressed separately. The new tolerance for green forage, will be 4 ppm, of which not more than 3 ppm is chlorpyrifos. For alfalfa hay, the tolerance will be 15 ppm, of which not more than 13 ppm is chlorpyrifos (memo, S.H. Willet, 3/9/88). However, TOX has stated (A. Levy, 11/29/88) that TCP is no longer considered to be of toxicological concern.

**DETAILED CONSIDERATIONS**

**Proposed Use**

Although Lock-On\* is not currently registered for use on alfalfa, the active ingredient, chlorpyrifos, is registered through the use of Lorsban\*4E (EPA Reg. No. 62719-23). Lorsban\*4E is used to control a wide range of insects on alfalfa with a maximum dosage of 1.0 lb a.i./acre for a single application. The pregrazing and



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preharvest interval (PHI/PGI) varies with the dosage--21 days for >0.5 lb a.i./acre (1-2 pts. of Lorsban<sup>4E</sup>), 14 days for 0.5 lb a.i./acre (1 pt.), and 7 days for 0.25 lb a.i./acre (0.5 pts). The label specifies a maximum of 4 applications per year, and one per crop cutting. Chlorpyrifos constitutes 40.7% of the Lorsban<sup>4E</sup> formulation (4 lb a.i./gal).

DowElanco requests a 4-day PHI/PGI for the use of Lock-On<sup>\*</sup> on alfalfa. The proposed single application rate is 0.38-0.5 lb a.i./acre. Chlorpyrifos constitutes 22.9% of the Lock-On<sup>\*</sup> formulation (2 lb a.i./gal). The proposed amendments would only be applicable in Arizona and California.

### Nature of the Residue

The metabolism of chlorpyrifos in plants and animals is adequately understood (memo S.H. Willet, 9/23/88). The residues of concern, and those determined in the subject study, had been the parent, chlorpyrifos, and the metabolite 3,5,6-Trichloro-2-pyridinol (TCP). However, the S. Bacchus memo of 3/22/91 states that TCP is no longer considered to be of toxicological concern and that a tolerance expression excluding TCP would be acceptable.

### Analytical Method

The methods used were: Method ACR 78.10, "Determination of Residues of Chlorpyrifos in Alfalfa by Gas Chromatography," J.H. Walters, 1978 (unpublished residue method of DowElanco); and Method ACR 84.4, "Determination of Chlorpyrifos and 3,5,6-Trichloro-2-pyridinol in Stone Fruit by Gas Chromatography," Miller and McKeller, 1984 (unpublished residue method of DowElanco). Duplicate samples are analyzed. Method ACR 78.10 is used to determine chlorpyrifos residues. Subsequently, Method ACR 84.4 is used, in which any chlorpyrifos present is hydrolyzed to TCP. Residues of TCP are determined by difference. The methods have been used in previous submissions (PP#3F2884).

In method ACR 78.10, alfalfa samples are extracted with acetone and centrifuged. An aliquot of the supernatant is transferred to a volumetric flask and brought to volume with acetone. A portion of this sample is subjected to gas chromatography with flame photometric detection. The lower limit of quantitation (LOQ) for the method is 0.5 ppm chlorpyrifos.

A duplicate sample is treated according to method ACR 84.4. Residues extracted from alfalfa by shaking with hot methanolic sodium hydroxide. An aliquot of the extract is evaporated until only water remains. The aliquot is acidified and cleaned up on a C<sub>18</sub> Sep-Pak. The TCP is eluted with methanol into benzene and partitioned with sodium bicarbonate. The sodium bicarbonate is acidified and back partitioned with benzene. The TCP in the benzene phase is derivatized with N,O-bis(trimethylsilyl)acetamide

to form the pyridinol trimethylsilyl derivative, which is then quantitated by gas chromatography with electron capture detection. The LOQ is 1.0 ppm TCP.

Fortifications were performed at 0.5, 1, 2, 4, and 5 ppm for chlorpyrifos, with an average recovery of 96% (n=15). Fortifications were performed at 1, 2, and 4 ppm for TCP, with an average recovery of 86% (n=7). There was no indication whether the recoveries were for green forage or cured hay of alfalfa. All analytical work was conducted by A & L Great Lakes Agricultural Laboratories.

### Storage Stability

Previously submitted storage stability data (PP#3F2884) showed 78% recovery of chlorpyrifos (340 days) and 70% recovery of TCP (346 days) in green forage. For cured alfalfa hay, there was 105% recovery of chlorpyrifos (340 days) and 74% recovery for TCP (346 days).

### Magnitude of the Residue

New residue data were submitted by DowElanco to support the proposed label amendment for Lock-on\* (MRID No. 417390-01). Alfalfa test plots in California were treated with a single postplant application of Lorsban\*2E at rates of 0.25 and 0.50 lb a.i./acre. Samples of green forage and cured hay were collected 3-4, 7-8, and 14 days after application of the insecticide. Hay samples were dried for 3 days in the field. Green forage samples were chopped with a Hobart food cutter and stored frozen. Cured hay samples were ground in a model 4 Wiley mill to 4 mm and then stored frozen. Samples were stored <3 months.

Residues of chlorpyrifos and TCP in both green forage and cured alfalfa hay are shown below.

Rate (lb a.i./A)	Type	Treatment to Sampling (Days)	Chlorpyrifos Residues (ppm, n=4) <sup>a</sup>	TCP Residues (ppm, n=4) <sup>b</sup>
0.25	Green Forage	4	<0.5 - 0.69	<0.5
		8	<0.25 - <0.5	<0.5
		14	<0.25 - <0.5	<0.5
	Hay	7	<0.25 - <0.5	<0.5
		10	<0.25	<0.5
		17	<0.5 - 0.69	<1.0 - 1.0
0.50	Green Forage	4	<0.5 - 1.7	<0.5 - <1.0
		8	<0.25 - 1.5	<0.5 - <1.0
		14	<0.50 - 0.71	<0.5 - <1.0
	Hay	7	<0.25	<0.5
		10	0.74 - 1.3	2.4 - 3.0
		17	1.0 - 1.2	<1.0 - 2.3

<sup>a</sup>LOQ = 0.5 ppm; registrant considered nondetectable to be  
1/2 LOQ = 0.25 ppm

<sup>b</sup>LOQ = 1.0 ppm; registrant considered nondetectable to be  
1/2 LOQ = 0.5 ppm.

The residue data support the use of Lock-On\* for alfalfa. The proposed maximum application rate, 0.5 lb a.i./acre, is half the maximum application rate (1.0 lb a.i./acre) for Lorsban\*4E.

The Lorsban\*4E label indicates a 14-day PHI for an application rate of 0.5 lb a.i./acre. The proposed PHI for the same rate, using the Lock-On\* product, is 4 days. The residue data submitted indicate that chlorpyrifos and TCP residues well below established tolerances will remain on green alfalfa forage after 4 days, and on cured alfalfa hay after 7 days. After 10 days and 17 days, chlorpyrifos and TCP residues on alfalfa hay showed a slight increase for the proposed application rate, but also remained below established tolerances.

#### Meat, Milk, Poultry, and Eggs

Tolerances for combined residues of chlorpyrifos and TCP in meat, milk, poultry and eggs have been established. The proposed

use of Lock-On\* is not likely to create residues exceeding the established tolerances.

#### CBRS Comments

1. The nature of the residue is adequately understood.
2. An analytical method exists which can be used for data collection and enforcement purposes.
3. The proposed use of Lock-On\* on alfalfa indicates dosages of the active ingredient currently in use for Lorsban\*4E. For the purpose of this request, residue data generated from test plot treatments with Lorsban\*2E, a former name for Lock-On\*, can be used to support the proposed label amendment for Lock-On\*.
4. Lock-On\* and various formulations of Lorsban\* contain the same active ingredient, chlorpyrifos, and are all emulsifiable concentrates. The various product formulations can be considered equivalent, on the basis of the active ingredient, for residue studies.
5. Fortification data submitted with the request for label amendment did not indicate which type of alfalfa had been used (green forage or cured hay). DowElanco should clarify which type of alfalfa samples were used in the studies. Fortification studies should have been performed on both green forage and cured hay alfalfa.
6. Given that California and Arizona do not constitute a large portion of the alfalfa growing region in the U.S., the test plot in California used in the studies submitted in support of the amended label request is deemed to be representative of the region specified in the proposed amended label.
7. The residue data submitted with the request indicate that the proposed use will not generate residues exceeding established tolerances for chlorpyrifos and TCP at a PHI/PGI of 4 days.

#### Conclusions

CBRS could recommend approval of the requested label amendment, provided DowElanco addresses the concern regarding fortification data (CBRS comment #5, listed above).

cc: CBSwartz (CBRS), Circulate (7), RF, Chlorpyrifos SF, Amended Use File

H7509C:CBRS:CBSwartz:CM#2:Rm 800D:703-557-2877:3/27/91

RDI:WJHazel: 4/3/91

EZager: 4/3/91